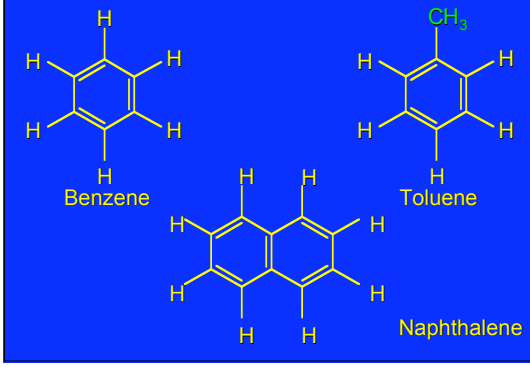
Arenes and Aromaticity

Examples of Aromatic Hydrocarbons



Benzene

Some history

1825 Michael Faraday isolates a new hydrocarbon from illuminating gas.

1834 Eilhardt Mitscherlich isolates same substance and determines its empirical formula to be C_nH_n. Compound comes to be called *benzene*.

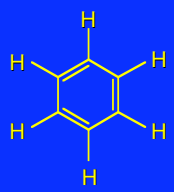
1845 August W. von Hofmann isolates benzene from coal tar.

1866 August Kekulé proposes structure of benzene.

Kekulé and the Structure of Benzene

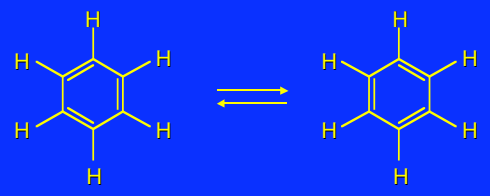
Kekulé Formulation of Benzene

Kekulé proposed a cyclic structure for C_6H_6 with alternating single and double bonds.



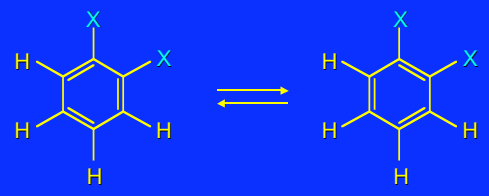
Kekulé Formulation of Benzene

Later, Kekulé revised his proposal by suggesting a rapid equilibrium between two equivalent structures.



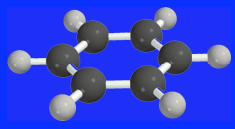
Kekulé Formulation of Benzene

However, this proposal suggested isomers of the kind shown were possible. Yet, none were ever found.



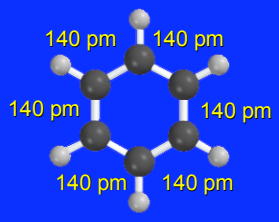
Structure of Benzene

Structural studies of benzene do not support the Kekulé formulation. Instead of alternating single and double bonds, all of the C—C bonds are the same length.

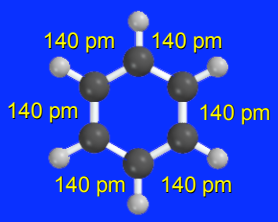


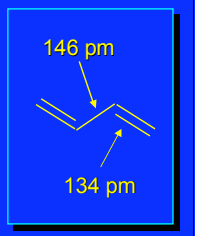
Benzene has the shape of a regular hexagon.

All C—C bond distances = 140 pm



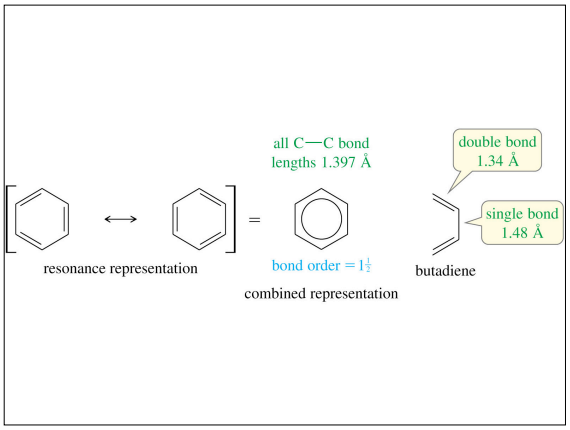
All C—C bond distances = 140 pm

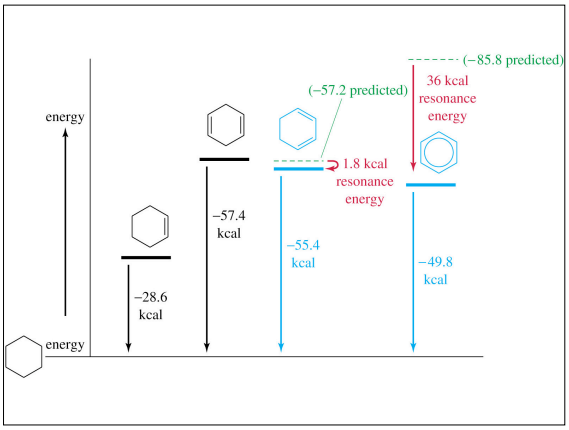




140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.

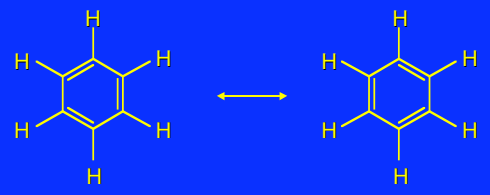
A Resonance Picture of Bonding in Benzene





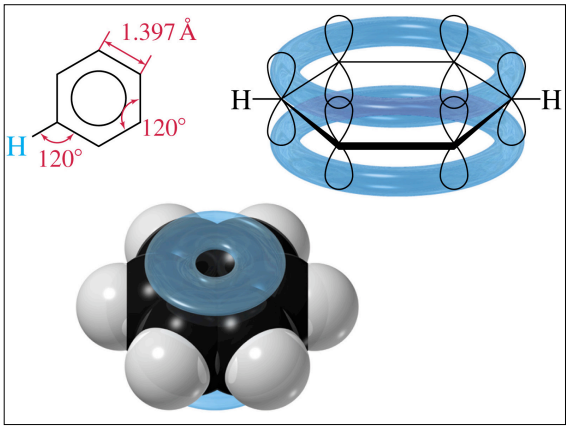
Resonance Formulation of Benzene

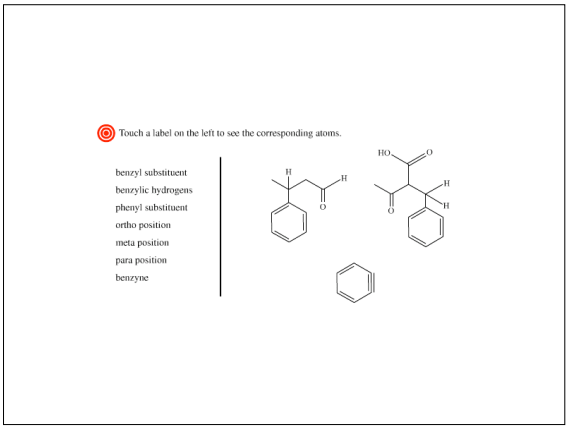
express the structure of benzene as a *resonance hybrid* of the two Lewis structures. Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbons.



Resonance Formulation of Benzene

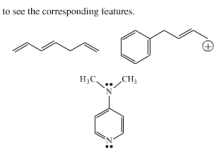
Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two Kekulé structures)





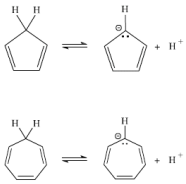
Touch a label on the left to see the corresponding features.

allylic cation
aromatic rings
benzylic carbon
conjugated double bonds
delocalized lone pair
localized lone pair

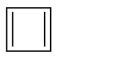


Acid Strength & Aromaticity

In this exercise, you will systematically compare the acidities of the two cyclic hydrocarbons on the left. Click "Start" to begin.

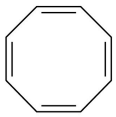


Start

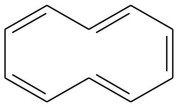


cyclobutadiene
[4]annulene

benzene
[6]annulene



cyclooctatetraene
[8]annulene



cyclodecapentaene
[10]annulene

The π Molecular Orbitals of Benzene

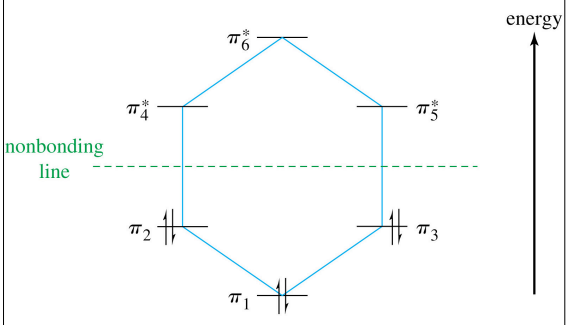
Benzene MOs

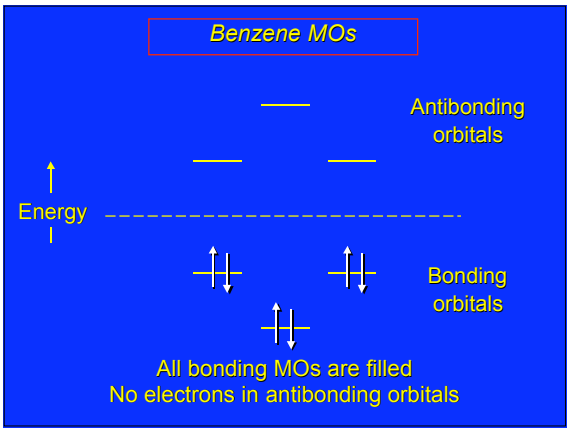
Antibonding orbitals

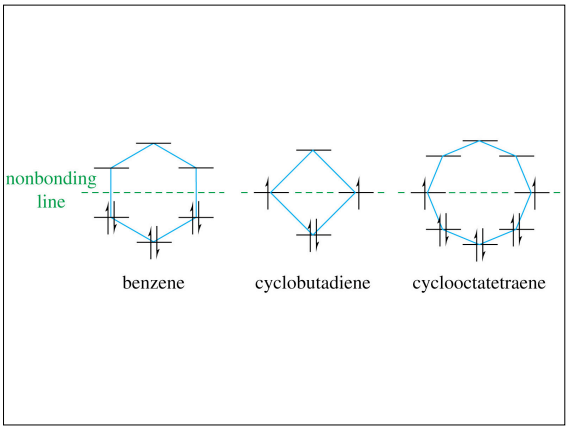
Energy

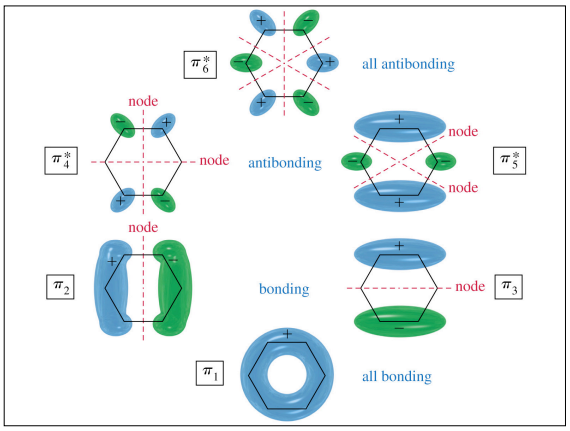
Bonding orbitals

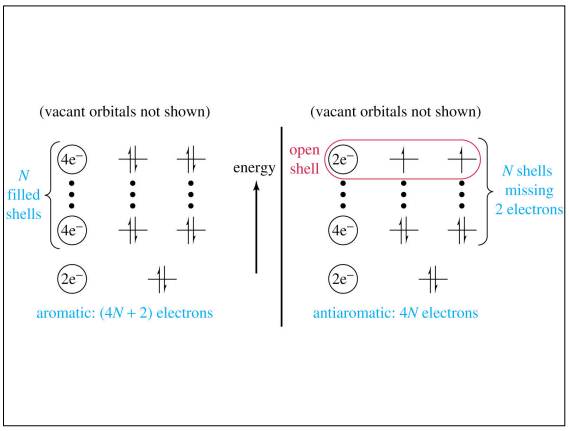
6 *p* AOs combine to give 6 π MOs
3 MOs are bonding; 3 are antibonding





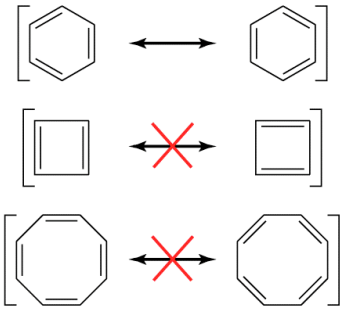






Aromatic vs. "anti-aromatic"

A. Deniz, et. al., *Science*, 5 November 1999



11.19
Hückel's Rule:
Annulenes

the additional factor that influences aromaticity is the number of π electrons

Hückel's Rule

among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2$ π electrons possess special stability (are aromatic)

n	$4n+2$
0	2
1	6
2	10
3	14
4	18

Hückel's Rule

among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2$ π electrons possess special stability (are aromatic)

n	$4n+2$	
0	2	
1	6	benzene!
2	10	
3	14	
4	18	

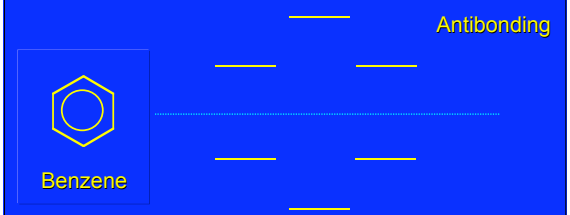
Hückel's Rule

Hückel restricted his analysis to planar, completely conjugated, monocyclic polyenes

he found that the π molecular orbitals of these compounds had a distinctive pattern

one π orbital was lowest in energy, another was highest in energy, and the others were arranged in pairs between the highest and the lowest

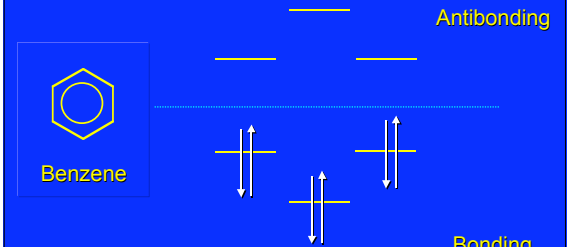
π-MOs of Benzene



6 *p* orbitals give 6 π orbitals

3 orbitals are bonding; 3 are antibonding

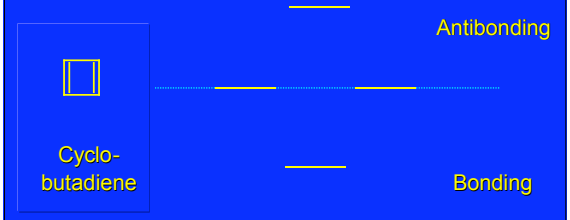
π-MOs of Benzene



6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

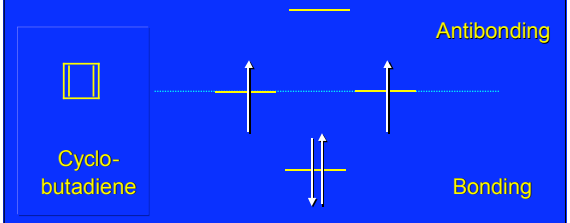
π-MOs of Cyclobutadiene (square planar)



4 *p* orbitals give 4π orbitals

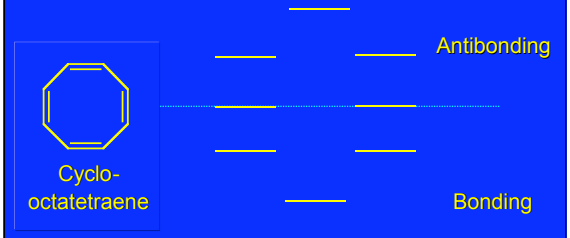
1 orbital is bonding, one is antibonding, and 2 are nonbonding

π-MOs of Cyclobutadiene (square planar)



4 π electrons; bonding orbital is filled; other 2 π electrons singly occupy two nonbonding orbitals

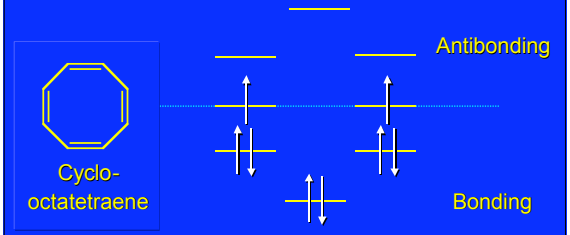
π-MOs of Cyclooctatetraene (square planar)



8 *p* orbitals give 8 π orbitals

3 orbitals are bonding, 3 are antibonding, and 2 are nonbonding

π-MOs of Cyclooctatetraene (square planar)



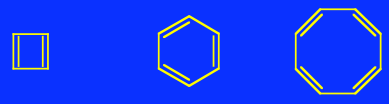
8 π electrons; 3 bonding orbitals are filled; 2 nonbonding orbitals are each half-filled

π-Electron Requirement for Aromaticity

4 π electrons — not aromatic

6 π electrons — aromatic

8 π electrons — not aromatic

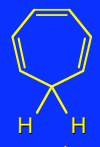


Completely Conjugated Polyenes

6 π electrons; completely conjugated

aromatic

6 π electrons; not completely conjugated

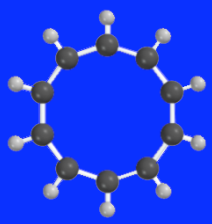


not aromatic

Annulenes

Annulenes are planar, monocyclic, completely conjugated polyenes. That is, they are the kind of hydrocarbons treated by Hückel's rule.

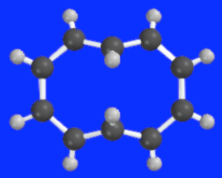
[10]Annulene



predicted to be aromatic by Hückel's rule, but too much angle strain when planar and all double bonds are cis

10-sided regular polygon has angles of 144°

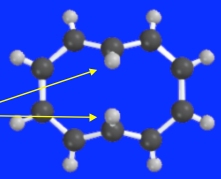
[10]Annulene



incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity

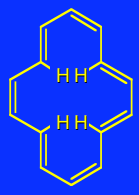
[10]Annulene

van der Waals strain between these two hydrogens



incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity

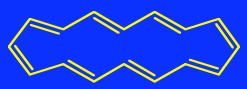
[14]Annulene



14 π electrons satisfies Hückel's rule

van der Waals strain between hydrogens inside the ring

[16]Annulene

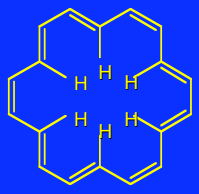


16 π electrons does not satisfy Hückel's rule

alternating short (134 pm) and long (146 pm) bonds

not aromatic

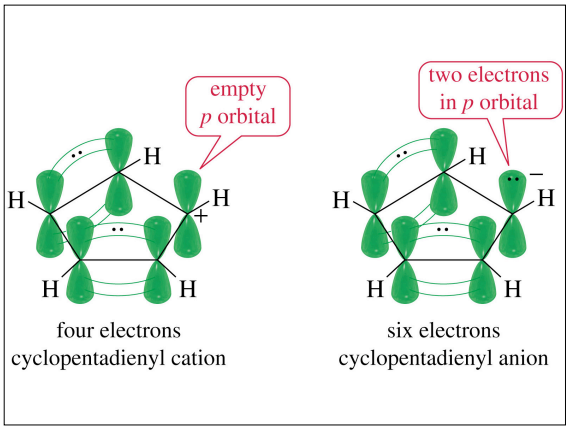
[18]Annulene

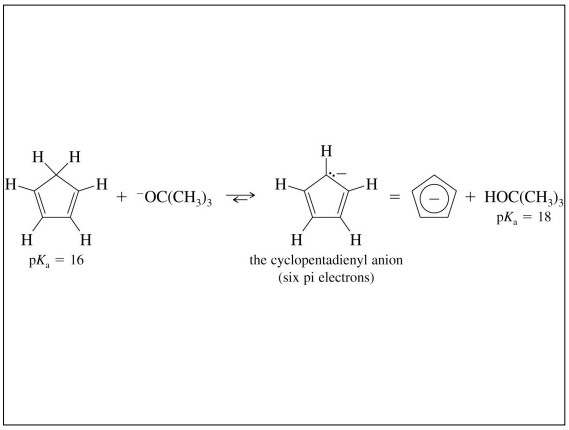


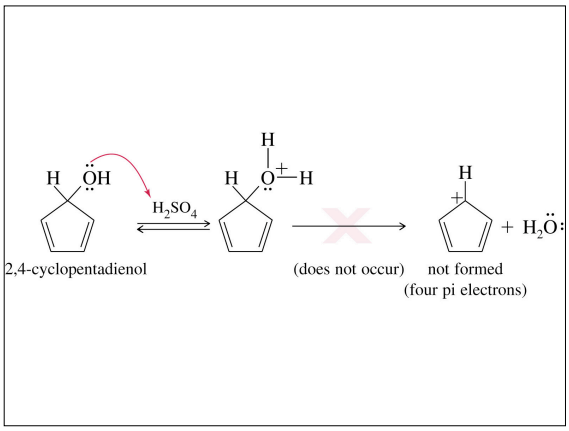
18 π electrons satisfies Hückel's rule

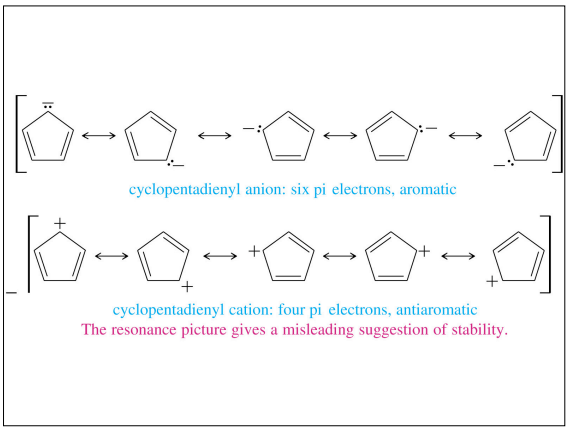
resonance energy = 418 kJ/mol

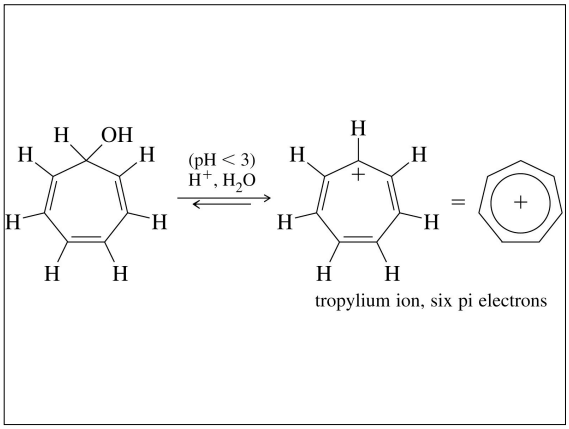
bond distances range between 137-143 pm

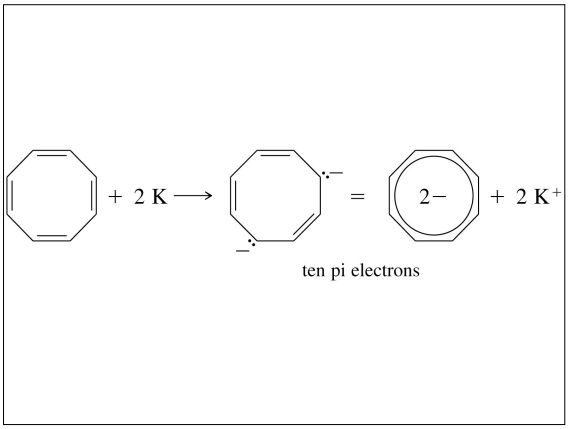

empty
p orbital
two electrons
in p orbital
four electrons
cyclopentadienyl cation
six electrons
cyclopentadienyl anion


pKa = 16
the cyclopentadienyl anion
(six pi electrons)
pKa = 18

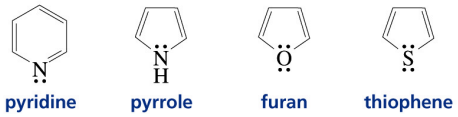

H2SO4
2,4-cyclopentadienol
(does not occur)
not formed
(four pi electrons)


cyclopentadienyl anion: six pi electrons, aromatic
cyclopentadienyl cation: four pi electrons, antiaromatic
The resonance picture gives a misleading suggestion of stability.


(pH < 3)
H+, H2O
tropylium ion, six pi electrons


+ 2 K
2−
+ 2 K+
ten pi electrons

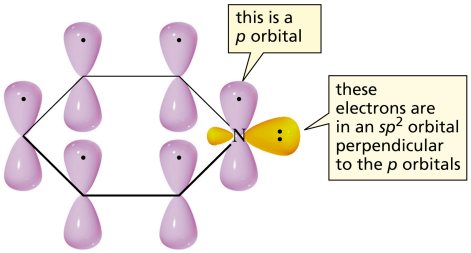
Aromatic Heterocyclic Compounds



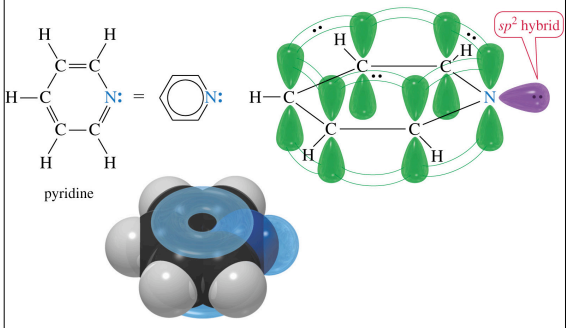
pyridine **pyrrole** **furan** **thiophene**

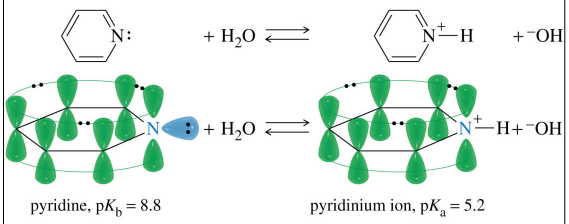
A heterocycleis a cyclic compound in which one or more of the ring atoms is an atom other than carbon.

Pyridine Is Aromatic

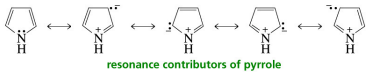


orbital structure of pyridine

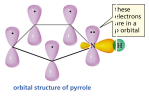




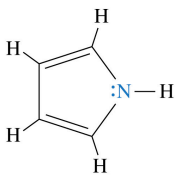
Pyrrole Is Aromatic



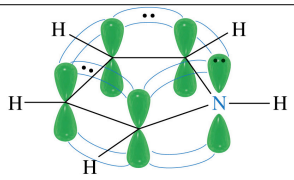
resonance contributors of pyrrole



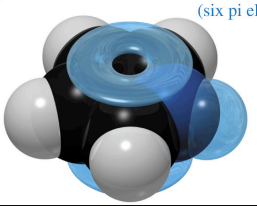
orbital structure of pyrrole

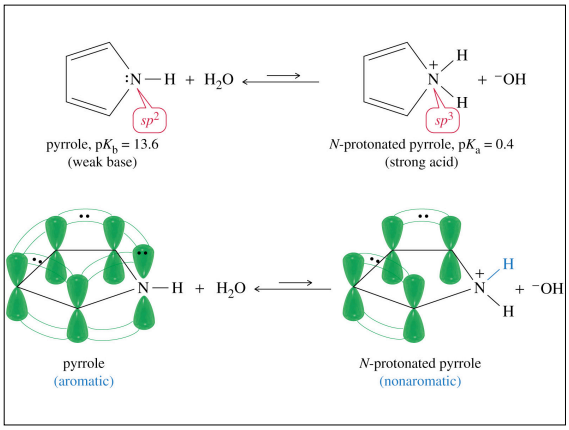


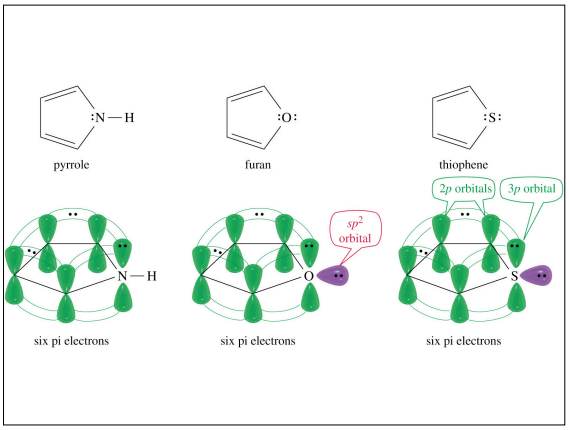
pyrrole



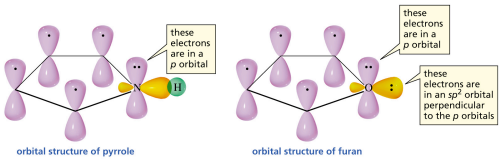
orbital structure of pyrrole
(six pi electrons, aromatic)

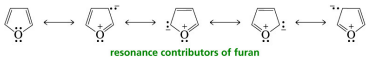




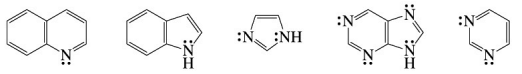


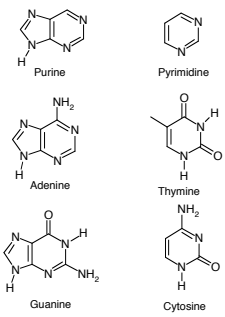
Furan Is Aromatic





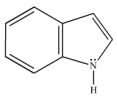
Examples of Important Nitrogen Heterocyclic Aromatic Compounds





HÜCKEL'S (4n + 2) RULE

The object of this exercise is to identify the number of pairs of π electrons to check for aromaticity. Click on the pairs of π electrons that make up the aromatic system, and then click "Done".

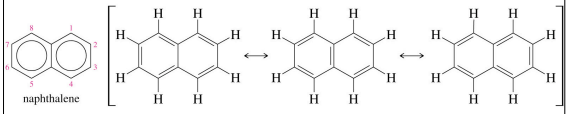


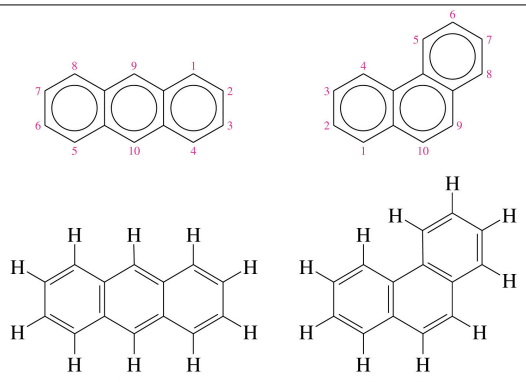
Done

Aromatic/ Antiaromatic/ Non-aromatic

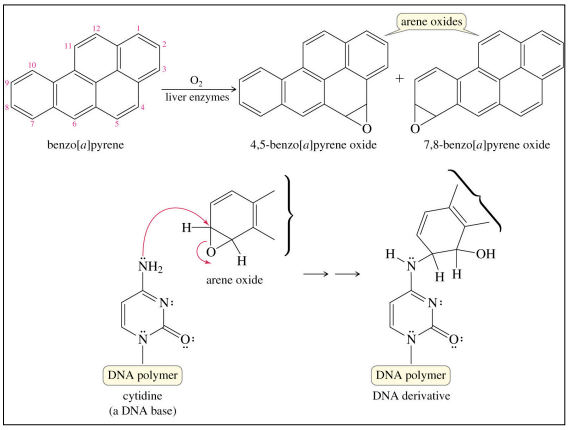
Click as to whether the following molecule is aromatic, antiaromatic, or neither.

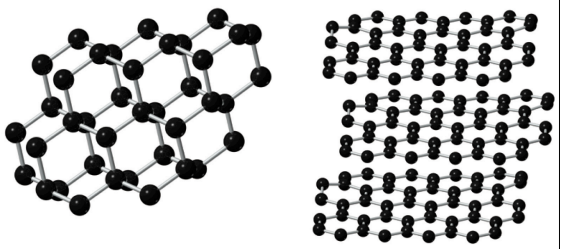
Aromatic | Antiaromatic | Neither

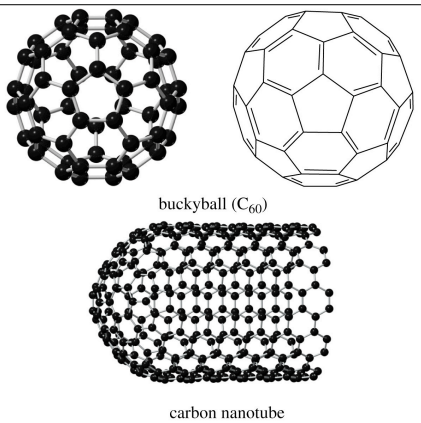


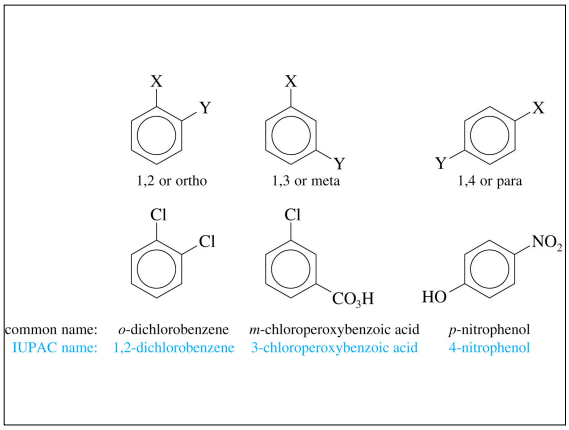


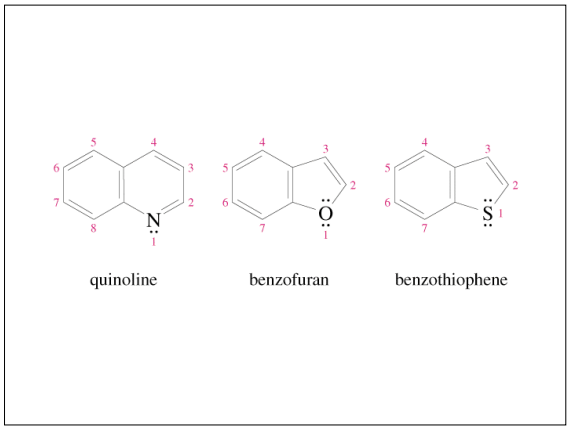
(Only one Kekulé structure is shown for each compound.)

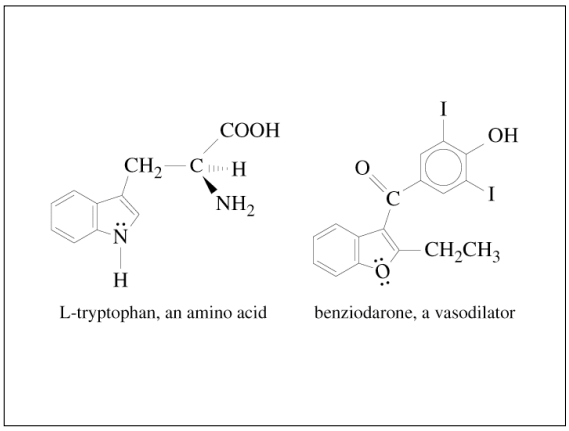


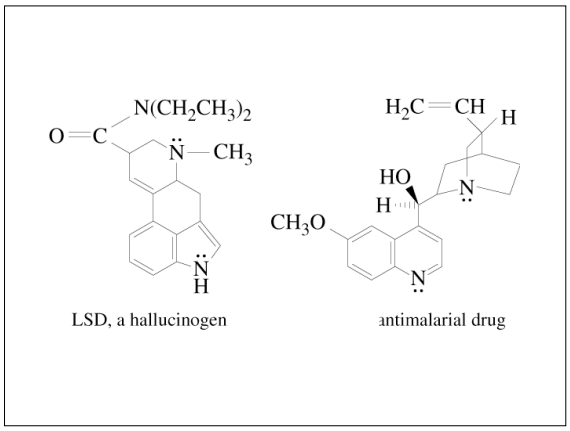


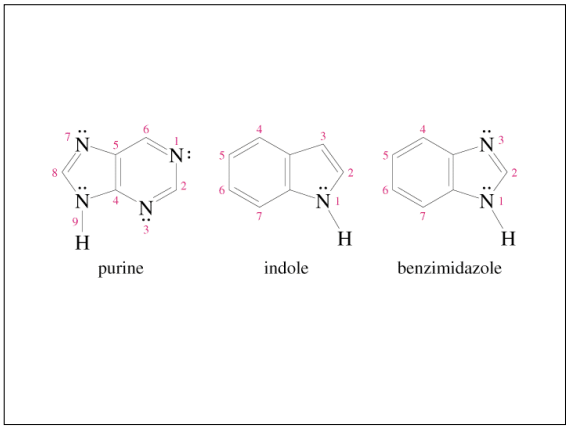


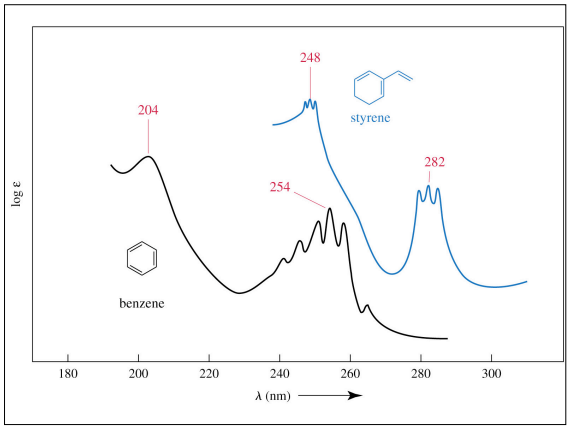

1,2 or ortho
1,3 or meta
1,4 or para
common name: o-dichlorobenzene m-chloroperoxybenzoic acid p-nitrophenol
IUPAC name: 1,2-dichlorobenzene 3-chloroperoxybenzoic acid 4-nitrophenol

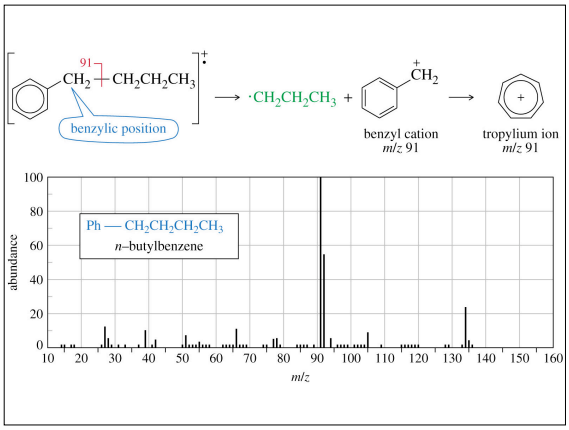

quinoline
benzofuran
benzothiophene


L-tryptophan, an amino acid
benziodarone, a vasodilator


LSD, a hallucinogen
antimalarial drug


purine
indole
benzimidazole


log ε
204
248
254
282
styrene
benzene
180
200
220
240
260
280
300
λ (nm)


91
CH2 CH2CH2CH3
benzylic position
·CH2CH2CH3 +
CH2
benzyl cation
m/z 91
tropylium ion
m/z 91
100
80
60
40
20
0
abundance
Ph — CH2CH2CH2CH3
n–butylbenzene
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
m/z